CrossMark

Synthesis of high-value organic acids from sugars promoted by hydrothermally loaded Cu oxide species on magnesia

Hemant Choudhary, Shun Nishimura, Kohki Ebitani *

School of Materials Science, Japan Advanced Institute of Science and Technology (JAIST), 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan

A B S T R A C T

Design of a suitable catalyst for the conversion of inedible-biomass, a renewable resource, into high-value chemicals is an immense and important area of research in an era of energy crisis. This paper demonstrates batch conversion of sugars into lactic acid (LA) and formic acid (FA) employing a supported copper catalyst. A magnesia-supported copper catalyst was synthesized by a hydrothermal methodology using CTAB as the capping agent (denoted as CuCTAB/MgO). We found that the CuCTAB/MgO not only dramatically boosted the yields of LA and FA from sugars but also decreased the energy demand of the process by decreasing the reaction temperature from 523 K to 393 K. The high yields of LA (70%) in the presence of NaOH and of FA (65%) in the presence of H_2O_2 were achieved from glucose at 393 K in water using a CuCTAB/MgO catalyst, which could be recycled without any significant loss of activity. The copper catalyst was also found to exhibit excellent activity for the transformation of other sugars. The catalyst was characterized using PXRD, H_2-TPR, N_2 adsorption–desorption, and other analytical techniques to investigate the active Cu species and propose a plausible mechanistic pathway to LA.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The demanding consumption of non-renewable fossil fuels has increased CO_2 concentrations in the environment. Depleting resources and increasing environmental concerns are inspiring researchers to develop renewable sources for a sustainable and stable future. The potential to use biomass as a substitute for the conventional petroleum feedstock has been known and realized in the past few years [1,2]. In principle, the uses of biomass could be more diverse than for crude oil; however, realization of this is challenging. Currently, both academic and industrial professionals are striving to convert cellulosic or lignocellulosic biomass into commodity chemicals at higher efficiencies. A variety of chemicals, such as 5-hydroxymethyl-2-furaldehyde [3], 2-furaldehyde [3], 2,5-dimethylfuran [4], 2,5-diformylfuran [5], succinic acid [6], levulinic acid [7], fatty acids and alcohols [8], and lactic acid (LA) [9], can be produced from biomass by engineering suitable catalysts and reaction conditions. Among these commodity chemicals, LA has attracted the most attention, and the direct conversion of sugars

into LA is highly desired. Formic acid (FA) is another organic acid of high interest to the researchers of this era, who are trying to harvest it in higher yields from renewable feedstock. LA is used extensively in detergents, antibacterial agents, cosmetics, food additives, and biodegradable plastics, whereas FA is used as a potential hydrogen donor and reserve [10,11]. The increasing global demand for high-value and high-energy chemicals emphasizes the importance of research on cellulosic biomass transformation.

The fermentation of sugars is the key process among potential candidates for syntheses of LA [12] and FA [13]. The industrial synthesis of LA is dominated by the fermentation method because of the increasing market demand for *bio*-LA [14]. The hydrolysis of methyl formate is currently the state of the art for FA, constituting approximately 49% of the total production capacity [15]. The fermentation processes are, however, expensive due to product purification, strict control of reaction conditions, and restricted large-scale operations. Water at higher temperatures has a unique property that eases the reaction pathway to such an extent that the use of a catalyst is not necessary. Inspired by this, many researchers have successfully converted carbohydrates into chemicals, mainly LA and formic acid (FA), with or without additives, as discussed later. The employment of extreme conditions of high temperatures and pressures to produce LA and FA in moderate yields opens up new areas of research to decrease energy demand for such severe processes. Moreover, the hydrothermal conditions at higher temperatures often decrease the selectivity, and thus a variety of
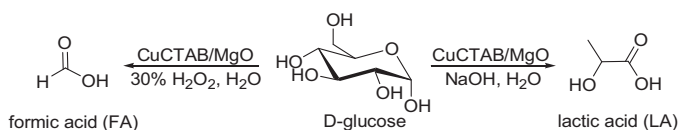
Scheme 1. Glucose conversions into LA and FA.

products are obtained, such as 5-hydroxymethyl-2-furaldehyde, organic acids, and char [16]. Herein, we have focused on the development of process technologies for the selective conversion of sugars to LA and FA under less extreme conditions using a catalyst.

Previous studies have reported the synthesis of LA from biomass under alkaline hydrothermal conditions or with acidic catalysts [9], producing LA in low to moderate yields. Although LA has long been known as an alkaline degradation product of sugars [17], extensive research regarding the improvement of the yields has occurred in recent years. Enomoto and others studied glycoaldehyde and glucose as substrates to synthesize LA in lower yields at higher temperatures [18]. As an improvement, they also reported that the use of sodium hydroxide (NaOH) and calcium hydroxide (Ca(OH)$_2$) could produce LA with 27% yield (from glucose) for shorter reaction times at 573 K [19]. Most reports in the literature focused on NaOH or Ca(OH)$_2$ for the alkaline hydrolysis of biomass. These results encouraged Esposito and Antonietti to investigate the effects of other bases; an impressive LA yield of 53% with homogeneous barium hydroxide (Ba(OH)$_2$) at 493 K for a longer reaction time was reported [20]. In contrast with the studies of LA production from biomass, very little has been reported regarding the direct formation of FA from biomass. Gao et al. successfully produced FA with 22% yield from pretreated cellulose at 483 K for 30 h [21]. A high yield of 75% FA was produced by Jin et al. at 523 K using 120% H$_2$O$_2$ from glucose [22]. Other studies report the formation of FA in trace amounts as a side product during LA synthesis.

The major disadvantage of the previous studies is that the operations occur at high temperatures (493–623 K) or yield low to moderate amounts of the desired organic acids. This disadvantage kindles the need for the development of a suitable catalyst or process for decreasing the energy demand involved in the alkaline hydrolysis of carbohydrates. Many researchers have focused on the role of earlier transition metals for improving the LA yields under alkaline hydrothermal conditions [23–25]. Onda et al. introduced calcined hydrotalcite as a heterogeneous base catalyst to obtain 20% LA yield from glucose [23]. Zhang et al. reported a 42% increase in the yields of LA from cellulose using Zn and Ni as co-catalysts [24]. In another recent study, the use of copper oxide in alkaline hydrothermal conversion was explored, improving the yields from 37–42% to 59% at 573 K [26]. The copper clusters synthesized under hydrothermal conditions were reported to exhibit superior activity for oxidation reaction compared with previous studies [27]. These achievements inspired us to synthesize hydrothermally loaded copper catalysts for high yields of organic acids via alkaline hydrolysis of saccharides.

In this study, we demonstrated the promotional effect of a hydrothermally loaded copper oxide species on magnesia using a capping agent (cetyltrimethylammonium bromide; CTAB) as an effective heterogeneous catalyst for the batch conversions of biomass-derived sugar into LA or FA in high yields under less extreme conditions (Scheme 1). In addition, the copper catalyst was found to be reusable with a simple reactivation by calcination, which is an advantage over the non-recyclable conventional methodologies involved for LA and/or FA synthesis from sugars. Moreover, in addition to glucose, other sugars including mono and disaccharides were also successfully converted into LA and FA using the supported copper catalyst. A plausible reaction pathway to LA

is proposed based on the characterization results, which identify the active Cu species.

2. Experimental

2.1. Chemicals

D(+)-glucose, starch (soluble), lactose monohydrate, sucrose, D(+)-raffinose pentahydrate, cetyltrimethylammonium bromide (CTAB), formic acid (FA), DL-glyceraldehyde, copper(I) oxide (Cu$_2$O), copper nitrate hexahydrate (Cu(NO$_3$)$_2$·6H$_2$O), and 30% hydrogen peroxide (H$_2$O$_2$) were purchased from Wako Pure Chemical Industries, Ltd. D(−)-fructose, D(+)-xylose, D(+)-cellobiose, acetic acid, magnesium oxide (MgO), sulfuric acid (H$_2$SO$_4$), and sodium hydroxide (NaOH) were procured from Kanto Chemical Co., Inc. Tokyo Chemical Industry Co. Ltd. supplied D(+)-galactose and glycolic acid, whereas DL-glyceric acid (GlycA) was bought from Nacalai Tesque Inc. L(+)-Lactic acid (LA) and pyruvaldehyde (PAL) were obtained from Sigma–Aldrich Co. LLC. Merck KGaA provided dihydroxyacetone (DHA) and microcrystalline cellulose. Strem Chemicals Inc. was the source for high purity (99.999%) copper(II) oxide (CuO).

2.2. Catalyst preparation

CTAB capped copper supported on magnesia (CuCTAB/MgO) was synthesized using a hydrothermal method described by Sarkar et al. with some modifications [27b]. CTAB, a cationic surfactant, was selected as the capping agent and dissolved in deionized water. In a typical synthesis methodology, MgO was dispersed in deionized water, and then an aqueous solution of Cu(NO$_3$)$_2$·6H$_2$O containing the requisite amount of copper was added dropwise into the solution under vigorous stirring. To this mixture, an aqueous solution of CTAB was added and vigorously stirred for 3 h. The obtained mixture was sealed in a 100 mL Teflon lined autoclave, heated to 453 K in an oven at a heating rate of 6 K min^{-1}, and maintained at the same temperature for 24 h. The oven was allowed to cool slowly to room temperature. The obtained solid was washed with deionized water until the pH of the filtrate became neutral; this was followed by washing with ethanol and then drying in vacuo overnight at room temperature. The dried materials were further calcined at 383, 573, 773, 973 or 1173 K with a ramp-rate of 10 K min^{-1} for 6 h in air. Various copper-loaded magnesia catalysts were denoted as xCuCTAB/MgO, where the x is the Cu content in mmol per gram of catalyst (mmol g^{-1}) in theory.

2.3. Catalytic testing

All experiments to test the catalytic activity were performed in a 50 mL Teflon lined autoclave. The catalytic activity was evaluated for conversion of glucose into LA or FA in aqueous media. In a general reaction procedure, glucose (or sugar) was dissolved in 5 mL deionized water. The catalyst was added to the solution, followed by the addition of NaOH solution or 30% H$_2$O$_2$ solution. The autoclave was sealed, purged with Ar (0.4 MPa), and mounted on a preheated oil bath at 373–413 K. The mixture was allowed to react for various time intervals with continuous magnetic stirring. After the reaction, a portion of the resultant solution was diluted 20 times with deionized water (or 10 mM H$_2$SO$_4$ for the samples containing alkali), and the catalyst was filtered off using a Milex®-LG 0.20 μm filter. The obtained filtrate was analyzed by high performance liquid chromatography (HPLC, WATERS 600) using an Aminex HPX-87H column (Bio-Rad Laboratories Inc.) attached to a refractive index detector. Aqueous 10 mM H$_2$SO$_4$ (as the mobile phase) was run through the column (maintained at 323 K) at a flow rate of 0.5 mL min^{-1}. The conversion and yield(s) were determined

using a calibration curve method from the equations below. The chemical name and structure for the expected/detected products are listed in Table S1. A typical HPLC chromatogram is shown in Fig. S1.

Recycling tests were performed to check the stability of the synthesized catalysts during the reaction. The catalyst was separated from the reaction mixture by centrifugation. The supernatant liquid was stored, and then analyses of the products and a leaching test of the catalysts were performed. The residual catalyst was washed through centrifugation with deionized water. Finally, the catalyst was dried *in vacuo* overnight and heated at 773 K for 6 h at a heating rate of 10 K min^{-1}. Fresh substrates and reagents were added to the catalyst, and then the reaction was performed again.

2.4. Calculation

The substrate conversion, product yields and carbon mass balance were calculated using the following equations:

$$\%\text{Conversion} = 100 - \left\{ \left(\frac{\text{Amount of saccharide detected (in mmol)}}{\text{Amount of saccharide used (in mmol)}} \right) \times 100 \right\}$$

$$\%\text{Product yield} = \left(\frac{\text{Number of carbon in product} \times \text{Amount of product detected (in mmol)}}{\text{Number of carbon in saccharide} \times \text{Amount of saccharide used (in mmol)}} \right)$$

$$\%\text{Carbon balance} = \left(\frac{\sum(\text{Yield of each product} \times \text{Number of carbon in each product})}{(\text{Conversion of saccharide} \times \text{Number of carbon in saccharide})} \right) \times 100$$

For xylose, because one molecule of xylose produces one molecule of LA, the calculation formulae were modified as shown. This calculation formula is supposedly one reason for the high activity of xylose in comparison with other monosaccharides.

$$\%\text{LA yield} = \left(\frac{\text{Amount of LA detected (in mmol)}}{\text{Amount of xylose used (in mmol)}} \right) \times 100$$

2.5. Characterization

Crystal structures were analyzed using powder X-ray diffraction (PXRD) with a SmartLab (Rigaku Co.) using Cu $K\alpha$ radiation ($\lambda = 0.154$ nm) at 40 kV and 30 mA in the range of $2\theta = 10$–$80°$. The diffraction patterns were analyzed using the database of the Joint Committee of Powder Diffraction Standards (JCPDS). Porosity and surface area were determined through a nitrogen adsorption–desorption method using a Brunauer–Emmett–Teller (BET) model in a BELSORP-max (BEL Jpn. Inc.). Sorption experiments were performed at liquid nitrogen temperature (77 K), and equilibration was allowed for each data point. All samples were pretreated at 373 K for 3 h under vacuum prior to the measurement. For inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis, an ICPS-7000 ver. 2 (Shimadzu Co.) was employed to quantify the actual amount Cu on MgO and to evaluate the Cu leaching, if any, during the reaction. The contents of Cu in the catalyst and/or the reaction medium were estimated using a calibration curve method. An H-7100 (Hitachi Ltd.) operating at 100 kV was used to acquire the morphology of the catalyst through a transmission electron microscopy (TEM) image. The samples for TEM measurements were dispersed in water, and the supernatant liquid was dropped onto a copper grid before drying *in vacuo* overnight. The electronic state of the Cu on MgO was analyzed by X-ray photoelectron spectroscopy (XPS). The experiments were conducted on an AXIS-ULTRA DLD spectrometer system (Shimadzu Co. and Kratos Analytical Ltd.) using an Al target at 15 kV and 10 mA in an energy range of 0–1200 eV. The binding energies were calibrated with the C 1s level (284.5 eV) as an internal standard reference. Temperature-programmed reduction (TPR) was performed with an Ohkura BP-2

instrument interfaced with a TCD. The TCD results were normalized to the mass of the used samples, and the rate of H$_2$ consumption was estimated based on the calibration curve of a pure CuO (99.999%) reduction. The TPR profile was recorded from 323 K under a H$_2$/Ar (5/95) flow at a ramping rate of 10 K min^{-1}. X-ray absorption spectroscopy (XAS) was performed with a transmission mode at a BL-9C in KEK-PF, with the approval of the Photon Factory Program Advisory Committee (Proposal No. 2013G586). All samples were grained and pressed into pellets with a diameter of 10 mm. Raman spectra were recorded on a T64000 (HORIBA Ltd.) to clearly demonstrate the particular oxide species present in the catalyst. The number of the Brønsted basic sites in MgO or CuCTAB/MgO was calculated by the titration method using benzoic acid. For instance, in an Erlenmeyer flask, 0.025 g of the catalyst was dispersed in 5 mL of a mixed solution (H$_2$O:EtOH (4:1; v/v)), and phenolphthalein was added as an indicator. Then, 0.05 M benzoic acid was added dropwise to the solution containing the sample, which was whirled until the discharge of pink color of the solution. The procedure was repeated to obtain concordant readings for each catalyst. The quantity of basic sites (mmol g^{-1}) was calculated as the ratio of consumed benzoic acid to the mass of the catalyst used.

3. Results and discussion

3.1. Catalytic activity

The catalytic activity of the synthesized catalyst was evaluated, and the reaction condition was optimized to achieve higher efficiencies for sugar transformation with glucose as the model compound. In this section, the catalytic activity for glucose transformation to LA and FA is described. The potential of the catalyst was further established by reusability experiments and testing with various other sugars.

3.1.1. Glucose conversion to LA

For a sustainable future, the conversion of sugars into LA in higher yields is an attractive topic to various researchers. We chose glucose as the model compound for optimization of reaction conditions to produce LA in high yields under milder conditions. In the conversion of glucose to LA, glyceric acid (GlycA) and glyceraldehyde (GlycAld) were the general by-products along with traces of acetic acid (AA), FA, and glycolic acid (GlcoA) in some cases. In 2008, Onda et al. reported the effect of calcination temperature on the activity of hydrotalcite as a solid base catalyst in the presence of alkali. The group reported a glucose conversion of 57% and a LA yield of 20%, employing 0.6 g of catalyst for 25 mmol L^{-1} of glucose in a 50 mmol L^{-1} NaOH solution. They found that the catalytic activity for LA depended linearly on the calcination temperature of hydrotalcite with increasing Brønsted basic sites [23].

We investigated the activity of CuCTAB/MgO calcined at various temperatures (383–1173 K) for glucose conversion to LA. As shown in Fig. 1, the activity for LA increased spontaneously for calcination temperatures of 383 K, 573 K and 773 K and decreased thereafter. Additionally, the number of Brønsted basic sites increased with
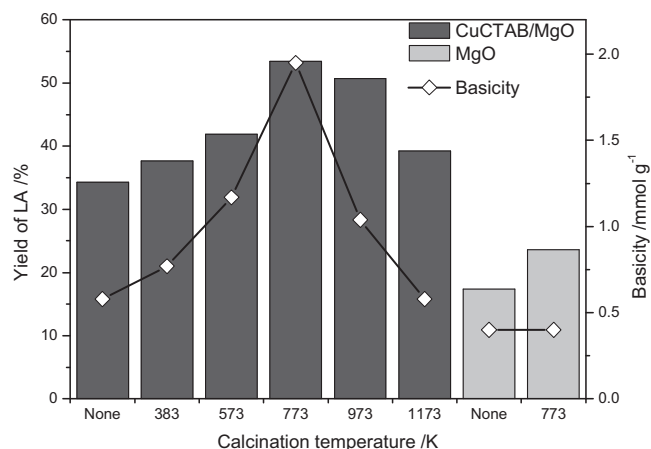
Fig. 1. Effect of the calcination temperature of CuCTAB/MgO on LA yields. Yields of LA for CuCTAB/MgO (dark gray columns) and MgO (light gray columns). Amount of basicity (◇). *Reaction conditions*: glucose (0.5 mmol, 90 mg), catalyst (1CuCTAB/MgO, 60 mg), water (5 mL), 1 M NaOH (1 mL), autoclave, Ar (0.4 MPa), 393 K, 1 h, stirring.

increasing calcination temperature, and then the number of basic site gradually decreased above 773 K, as also shown in Fig. 1. The MgO support alone possessed some activity, but it was less than for CuCTAB/MgO. The number of basic sites was found to be fewer

for MgO than for CuCTAB/MgO. Thus, the calcination temperature seemed to influence the basic sites [23] and/or the oxidation states of CuCTAB/MgO, thereby improving the yields of LA from glucose. CuCTAB/MgO calcined at 773 K exhibited the maximum number of Brønsted basic sites and maximum yield for LA (53.4%).

Fig. 2 describes the results of screening the conditions for LA synthesis from glucose over CuCTAB/MgO catalyst calcined at 773 K. Detailed information including the conversion of glucose, the yields of the by-products and the carbon mass balance are shown in Table S2 (see Supplementary data). An increase in the yield of LA was noted with increasing reaction temperature from 373 K to 413 K (Fig. 2a) as has been previously reported [18,19]. However, when the reaction temperature increased above 393 K, the yields for the smaller carbon-containing acids (GlcoA, FA and AA) increased with a decrease in carbon mass balance (Table S2). Some researchers have concluded that the highest LA yields *via* alkaline sugar degradation were obtained within a few seconds at higher temperatures [17–20,24,26], whereas others have reported that the deconstruction process at lower temperatures needs a longer reaction time in micro-reactors, less glucose, or more complex cellulosic material [20,21,23]. In the present study, the comparatively longer reaction time for high LA yields was essential due to the lower reaction temperatures. Below 623 K, the rate of LA formation from glucose is greater than the rate of decomposition of LA [19,28]. The rate of decomposition of LA also increased significantly at temperatures above 600 K [19]. In this study, the
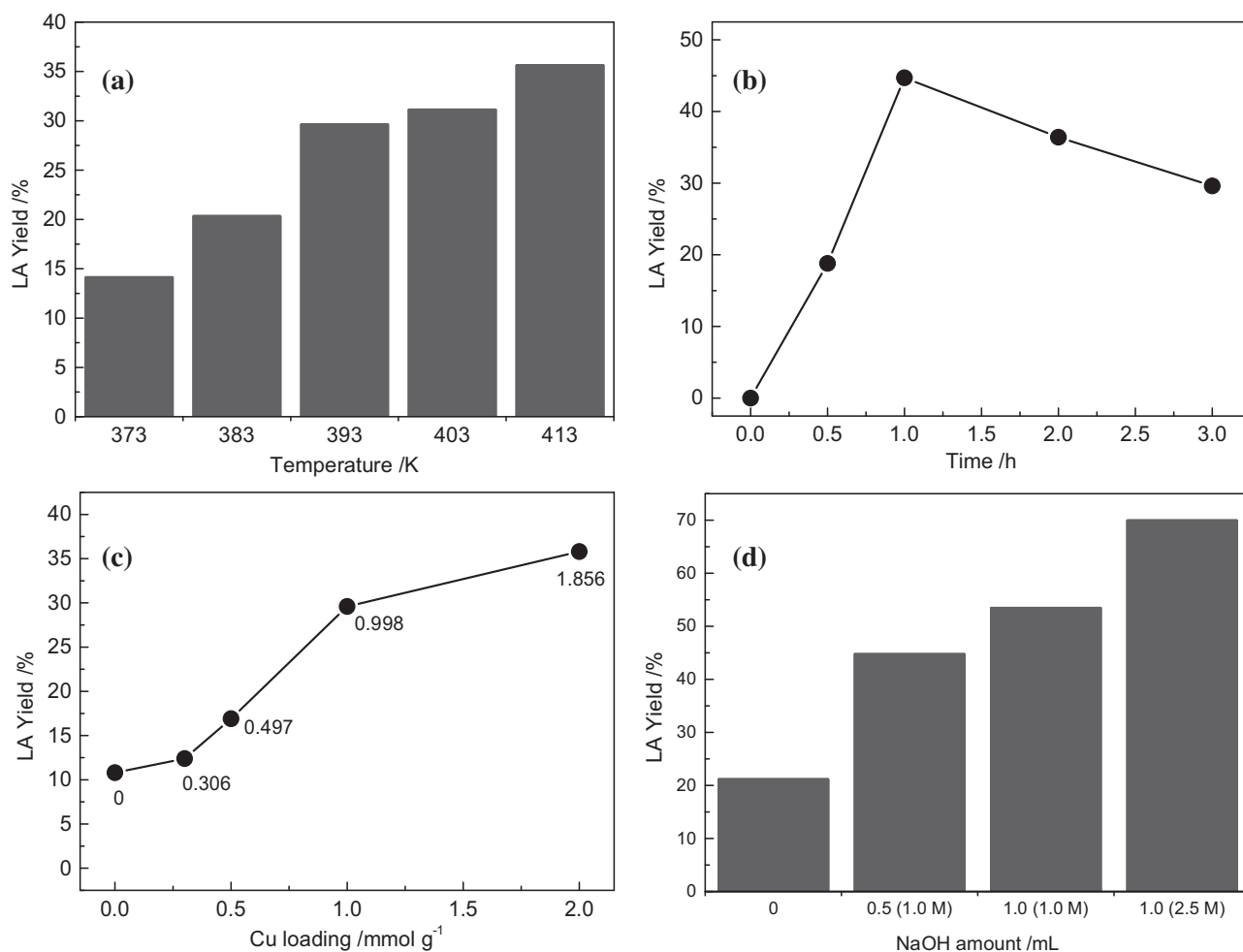

Fig. 2. Screening of the LA yields over the CuCTAB/MgO catalysts with different conditions. *Typical conditions*: glucose (0.5 mmol, 90 mg), catalyst (1CuCTAB/MgO calcined at 773 K; 60 mg), water (5 mL), 1 M NaOH (0.5 mL), autoclave, Ar (0.4 MPa), temp. (393 K), time (1 h,[d] 3 h[a,c]), stirring. The values in (c) displays the real amount of copper loading on magnesia as determined by ICP-AES. Plotted values were listed in Table S2 (see Supplementary data).

yields of LA increased gradually with increasing reaction time and decreased after 1 h at 393 K (Fig. 2b), which depends on the further breakdown of LA to smaller carbon containing compounds such as GlcoA and AA (observed in HPLC chart). Over-reaction of LA to GlcoA or AA was also detected in previous studies [21,26,28]. In addition, at a shorter reaction time (within 1 h), the LA yields were low even though glucose conversion reached 94.2%. GlycAld and GlycA dominated as the by-products in the reaction mixture at shorter intervals, whereas GlcoA, AA, and FA were the major by-products at longer reaction times (see Supplementary data for structure of by-products). Such results also indicated the decomposition of LA into smaller carbon-containing compounds at longer reaction times under the reaction conditions. Surprisingly, neither dihydroxyacetone (DHA) nor pyruvaldehyde (PAL) were detected at any stage of the reaction using the CuCTAB/MgO catalyst.

A synergistic effect of the catalyst and alkali existed under the reaction conditions. In the absence of either base or catalyst, lower activity for LA synthesis could be observed: 21.1% or 18.9% yield of LA, respectively; the yield is enhanced 3-fold in the presence of both the catalyst and base in the reaction (69.9% yield of LA). In these cases, the use of only the catalyst converted 88.7% glucose in comparison with >97.3% for only the base (see Table S2). Commercial CuO was used as a co-catalyst with NaOH (2.5 M, 1.0 ml) to verify the effect of bulk CuO on the yields of LA; nevertheless, the bulk CuO exhibited lower activity (32.3% yield) than the synthesized 1CuCTAB/MgO (69.9%) under the same conditions (see Table S2). These results establish the enhanced promotional effect of synthesized copper clusters over bulk copper [26,29]. Reaction of glucose at 393 K in water for 1 h yielded no products, which in turn reflects the potential of this catalytic system employed for LA synthesis. In contrast with the report by Wang et al. [26], the CTAB capped copper catalyst was selective for LA synthesis rather than AA. The lower temperatures of the experiments in addition to the nano-sized copper (*vide infra*; earlier reports utilized bulk copper as catalyst) could be among the reasons for these observed differences. The use of copper in the reaction decreased the by-products generally found for alkaline degradation of sugars under hydrothermal conditions (see Fig. S1). The possible metal–substrate interaction could account for the high selectivity that will be discussed later.

The catalysts with copper loadings in the range of 0.3–2 mmol g^{-1} were synthesized, and the catalytic efficiency was screened. As metal content increased from 0 to 2 mmol g^{-1}, the yield of LA correspondingly increased from 10.8% to 35.8% (Fig. 2c); however, these effects decreased with higher concentrations of copper; *i.e.*, increasing the copper loading from 0.998 to 1.856 mmol g^{-1} induced an increase in LA yield of only 6.2%. Moreover, the ICP-AES analysis of the reaction mixture indicated that leaching of copper species occurred in the case of 2CuCTAB/MgO calcined at 773 K (0.063 mmol L^{-1}), whereas no ionic copper (or leached copper) were observed for copper loading below 2 mmol g^{-1} in xCuCTAB/MgO after the reaction of glucose. Furthermore, a 1Cu/MgO catalyst without the capping agent calcined at 773 K (0.368 mmol g^{-1} Cu) possessed good catalytic activity (37.2% LA yield from glucose) (see Table S2), but leaching of metal species in the reaction medium was also observed by ICP-AES. Thus, the Cu species seemed to be easily and strongly stabilized onto the MgO in the presence of CTAB. CTAB has been known to favor high dispersion of metals such as Cu when used with metal oxides. Well-distributed copper clusters on the magnesia were observed throughout the CuCTAB/MgO catalyst calcined at 773 K (Fig. S2d). The effect of copper on the increased yields of LA from sugars has been previously suggested to be due to the *in situ* ionic copper formation [26]. The copper(II) ions were proposed to stabilize coordination with hydroxyl groups in glucose to ease the transfer of electrons from oxygen to copper, reducing it to copper(0). This electron donation would cleave glucose to
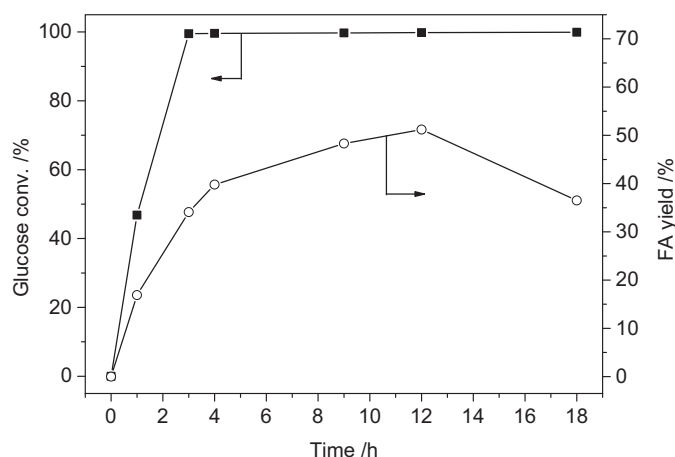

Fig. 3. Time course profile of FA formation. Glucose conversion (■), FA yield (○). *Reaction conditions*: glucose (0.5 mmol, 90 mg), catalyst (0.3CuCTAB/MgO calcined at 773 K, 60 mg), 30% H$_2$O$_2$ (2 mmol, 250 µL), water (5 mL), autoclave, Ar (0.4 MPa), 393 K, stirring.

LA and consequently convert LA to AA [26]. Fig. 2d displays the importance of the amount and concentration of alkali; the LA yield is maximized with 2.5 M NaOH, in accordance with the previous studies using NaOH [18–21,23,24,26]. Mechanistic studies of the alkaline degradation of sugars have portrayed aldol condensation, isomerization, keto-enol tautomerization and benzilic acid rearrangement as the crucial steps of the reaction path [18,28]. The basicity of the reaction medium hastens the rate of the above reactions, confirming the formation of LA as a function of base concentration. A similar trend and similar requirements for basic sites were observed in Figs. 1 and 2d, establishing the role of basicity in the present glucose conversion. The precise analyses of the reaction mixture using HPLC (Fig. S1) and NMR indicated that no polymerization occurred under our reaction conditions (see comments in Table S2 of Supplementary data).

3.1.2. Glucose oxidation to FA

In the past, few researchers have reported the formation of FA from the hydrothermal treatment of biomass [21,22,30]. Enomoto and others reported the difficulties in the synthesis of FA from sugars under hydrothermal conditions [22,31]. They utilized 120% H$_2$O$_2$ for FA production at 523 K for a shorter reaction time to achieve 24% FA yield. Other studies have reported the easy decomposition of FA under hydrothermal conditions or in the presence of excess H$_2$O$_2$, thereby suggested that suppression of the oxidative decomposition of FA significantly enhances the FA yield [31,32]. These results motivated us to investigate a new catalytic system for controlling the oxidative decomposition of FA, thereby increasing FA yields using less concentrated H$_2$O$_2$. For typical oxidation of glucose to FA, we found GlcoA and GlycA to be the only by-products.

The effect of copper loading on the FA yield from glucose was summarized in Table 1. The increase in copper loading on MgO from 0.1 to 0.3 mmol g^{-1} increased the FA yield (Table 1, entries 1–2). However, further increases in copper loading resulted in decreases in FA yield. (Table 1, entries 3–5). The Cu species with high loading may catalyze the FA decomposition. FA decomposition was confirmed by monitoring the time course of the FA yield (Fig. 3) [33]. An increase in the FA yield was found with the progress of the reaction, and the FA yield reached its peak at 12 h. Ideally, complete oxidation of glucose to FA requires six equivalents of oxygen [31]. Therefore, increased amounts of H$_2$O$_2$ with lower catalyst amounts were utilized; however, the yields were found to decrease (Table 1, entry 7). Finally, we found that the highest FA yield of 65% was achieved with increased amounts of low copper-loaded catalyst

Table 1
Effect of Cu loading on yields of FA.[a]

Entry	Catalyst[b]	Cu cont.[c] (mmol g^{-1})	Time (h)	Conv.[d] (%)	Yield[d] (%)			Carbon mass balance[e] (%)
					FA	GlycA	GlcoA	
1	0.1CuCTAB/MgO	0.103	3	97.4	22.8	16.8	10.1	16
2	0.3CuCTAB/MgO	0.306	3	>99	34.1	12.1	15.5	17
3	0.5CuCTAB/MgO	0.497	3	>99	30.6	15.2	16	18.2
4	1CuCTAB/MgO	0.998	3	>99	15.4	20.7	18.2	19.1
5	2CuCTAB/MgO	1.726	3	>99	8.5	29.3	22.1	23.5
6	0.3CuCTAB/MgO	0.306	12	>99	51.2	16.3	13.3	21.3
7[f,g]			12	>99	16.6	15.8	33.2	21.8
8[f,h]			12	>99	65	29	16.6	30.9
9	MgO (non-calcined)	0	3	82.9	4.7	4.4	12.5	8.6
10	Blank	0	12	20.6	4.9	7.1	2.3	25
11[i]	Blank	0	12	0.6	0	0	0	–

[a] *Reaction conditions*: glucose (0.5 mmol, 90 mg), Catalyst (60 mg), 30% H$_2$O$_2$ (2 mmol, 250 μL), Water (5 mL), Autoclave, Ar (0.4 MPa), 393 K, Stirring.
[b] Calcined at 773 K.
[c] Determined by ICP-AES.
[d] Calculated by HPLC analysis using the calibration curve method.
[e] Determined based on the observed products.
[f] 30% H$_2$O$_2$ (4 mmol).
[g] Catalyst (30 mg).
[h] Catalyst (90 mg).
[i] No 30% H$_2$O$_2$.

and high amounts of H$_2$O$_2$ (Table 1, entry 8). The potential role of the catalyst was ascertained by the blank reactions under similar reaction conditions with glucose; all of them showed little or no activity (Table 1, entries 10–11).

3.1.3. Reusability and viability of the catalyst

For any heterogeneous catalyst, the recyclability of the catalyst is one of the most important measures of its catalytic efficiency and stability. The retention of active sites and the prevention of metal leaching are the challenging aspects of these reactions. Previous studies utilizing Lewis acid catalyst for sugar degradation have demonstrated the efficient reusability of catalysts in organic solvents, whereas the activity is compromised in aqueous media [9c].

After the reaction, the catalyst was washed with water and recalcined at 773 K. The recalcined catalyst could be effectively reused for the conversion of glucose into LA and FA, as shown in Fig. 4. Moreover, ICP-AES analysis of the supernatant liquid of the reaction mixture after centrifugation confirmed that the active catalyst did not leach into the solution under the reaction conditions, implying the heterogeneous nature of the CuCTAB/MgO catalyst.

Along with efficient recyclability, an ideal catalytic system for sugar conversion should also have a wide scope of substrates with high activity. Various saccharides, including monosaccharides (*e.g.*, xylose and galactose), disaccharides (*e.g.*, cellobiose), trisaccharides (*e.g.*, raffinose), and polysaccharides (*e.g.*, cellulose and starch), were examined as substrates under the same reaction conditions, as shown in Fig. 5 (see calculations in Section 2.4). Interestingly, xylose (a monosaccharide containing five carbons) exhibited the highest yields for LA and FA among the other saccharides. In general, the activity of the catalyst for organic acid syntheses from saccharides decreased with increasing complexity in the structure of the substrates; *i.e.*, the catalytic activity decreased from monosaccharide to disaccharide to polysaccharide even under the optimized conditions for each. The polysaccharides were stable under the present catalytic system with no yields of LA and FA [34]. Based on the above results, we suppose that the present catalytic system could rupture the β1→4 type bonds present in the disaccharides (as in lactose). The α1→6 bonding in raffinose or the α1→2 bonding in sucrose may restrict the performance of the present catalyst, and thus, no products were obtained.

3.2. Catalyst characterization

To identify the actual phase of the catalyst and the nature of the copper species, the PXRD patterns of the catalysts were measured (Fig. 6). To understand the correlation of copper and MgO as influenced by the calcination temperature, the PXRD patterns for the CuCTAB/MgO catalyst calcined at various temperatures were obtained as in Fig. 6a–f. The PXRD of CuO, Cu$_2$O, MgO and the surfactant CTAB are shown in Fig. S3. No reflections of the crystalline MgO were observed for the non-calcined CuCTAB/MgO or the CuCTAB/MgO calcined at the lower temperatures of 383–573 K (Fig. 6a–c); however, the crystalline MgO phase becomes prominent with increased calcination temperatures (Fig. 6d–f). The oxide species of copper forms the active constituent of the synthesized catalyst with a variable concentration of both Cu$_2$O and CuO [35,36]. The peaks at 36.4° and 39.5° corresponding to the (0 0 2) and
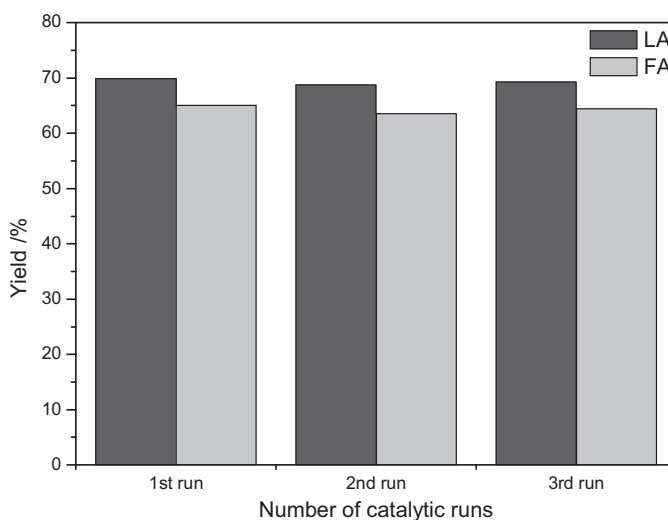

Fig. 4. Reusability of the catalyst for glucose conversion. Yields of LA (dark gray bars) and FA (light gray bars). *Reaction conditions for LA synthesis*: glucose (90 mg), catalyst (1CuCTAB/MgO calcined at 773 K, 60 mg), 2.5 M NaOH (1 mL), water (5 mL), autoclave, Ar (0.4 MPa), 393 K, 1 h, stirring. *Reaction conditions for FA synthesis*: glucose (90 mg), catalyst (0.3CuCTAB/MgO calcined at 773 K, 90 mg), 30% H$_2$O$_2$ (4 mmol, 500 μL), water (5 mL), autoclave, Ar (0.4 MPa), 393 K, 12 h, stirring.
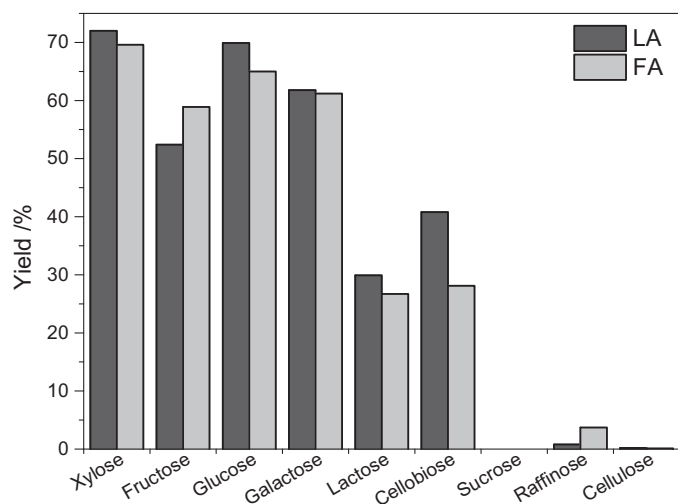
Fig. 5. Viability of the catalytic process for various saccharides. Yields of LA (dark gray columns) and FA (light gray columns). *Reaction conditions for LA synthesis:* saccharide (90 mg), catalyst (1CuCTAB/MgO calcined at 773 K, 60 mg), 2.5 M NaOH (1 mL), water (5 mL), autoclave, Ar (0.4 MPa), 393 K, 1 h, stirring. *Reaction conditions for FA synthesis:* saccharide (90 mg), catalyst (0.3CuCTAB/MgO calcined at 773 K, 90 mg), 30% H_2O_2 (4 mmol), water (5 mL), autoclave, Ar (0.4 MPa), 393 K, 12 h, stirring.
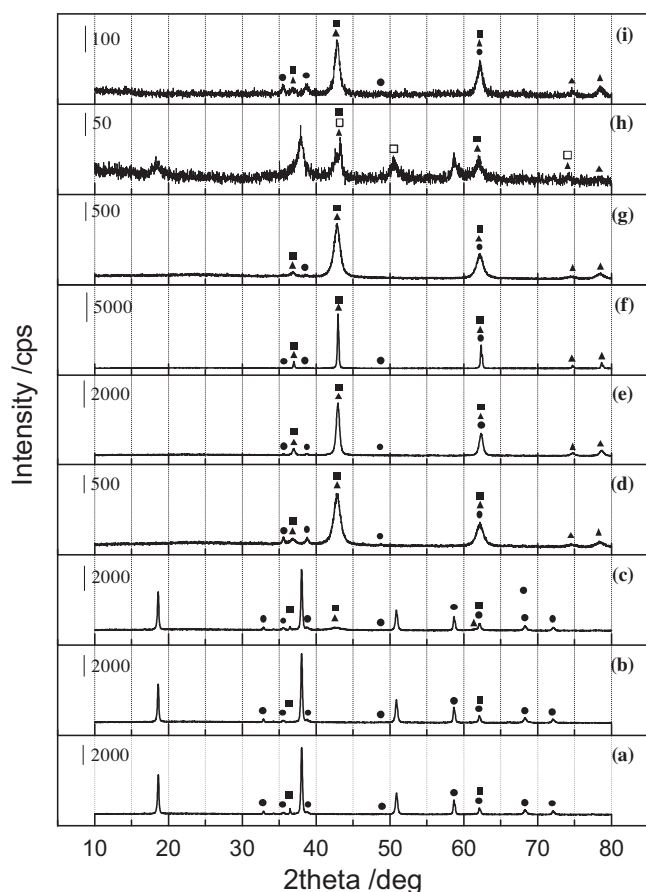

Fig. 6. PXRD patterns of the 1CuCTAB/MgO catalyst. The different species are shown as CuO (closed circle, ●); Cu_2O (closed square, ■); Cu (open square, □); and MgO (closed triangle, ▲). (a) Non-calcined CuCTAB/MgO; CuCTAB/MgO calcined at (b) 383 K, (c) 573 K, (d) 773 K, (e) 973 K and (f) 1173 K; (g) Cu/MgO calcined at 773 K; CuCTAB/MgO calcined at 773 K after (h) 1st use for LA synthesis from glucose, and (i) reactivation.

(2 0 0) planes of CuO revealed the presence of CuO crystallites for the catalyst calcined at 773 K (Fig. 6d). Although some CTAB was decomposed at high calcination temperatures and formed copper clusters, as observed in the TEM images (Fig. S2), the XRD patterns of the catalyst synthesized without CTAB (Cu/MgO) indicated the absence of any signals corresponding to the oxide phase of copper that was responsible for glucose conversion (Fig. 6d and g). The absence of activity for that catalyst (37.2% yield for LA synthesis; see Table S2) and the absence or low concentration of the copper oxide species observed in the PXRD patterns establish the crucial role of the copper oxide species as the active species in the CuCTAB/MgO catalyst for the production of organic acids from sugars.

The copper catalysts were found to be durable and to retain the active sites on recalcination as revealed by the PXRD patterns of the fresh and used catalysts in the LA synthesis (Fig. 6d, h and i). The observed patterns were interesting because the catalyst, following sugar conversion (Fig. 6h) formed structural sites (spinel type or mixed oxide phase) similar to those observed for the non-calcined catalyst (Fig. 6a) on the MgO phase. The peaks at 43.24° (1 1 1), 50.38° (2 0 0) and 74.28° (2 2 0), which were assigned to metallic copper (JCPDS; Cu: 04-0836), were observed after the reaction (Fig. 6h). The active species were regenerated on the recalcination of the catalyst (Fig. 6i). The X-ray absorption spectroscopy also indicated that the oxidized state of copper was present on the fresh CuCTAB/MgO catalyst, which contributed to the catalytic activity for the conversion of glucose, and that the reactivation treatment was effective for the reproduction of the active Cu species (see Figs. S4 and S5). We infer that CTAB strongly influenced the generation/regeneration of the active Cu species during calcination, and that effect was still retained within the structure even after repeated treatments at 773 K (Fig. S6).

Temperature-programmed reduction using hydrogen gas (H_2-TPR) is a common tool adopted by various researchers to investigate the dispersion and/or redox behavior of copper catalysts [37]. For better understanding of the copper phases on MgO, H_2-TPR profiles were recorded for the fresh catalysts (non-calcined 1CuCTAB/MgO, and 1CuCTAB/MgO calcined at 573 K, 773 K and 973 K) and the used catalysts (1CuCTAB/MgO calcined at 773 K after 1st use for glucose to LA and CuCTAB/MgO calcined at 773 K after reactivation) for comparison of the species and interactions in the catalyst. The presence of oxide species of copper in the catalyst was reflected in Fig. 7. Most of the profiles exhibited at least two peaks, indicating the different redox behavior of the present copper oxide species. Non-calcined CuCTAB/MgO had two peaks at 540 K, with a shoulder at 570 K and 685 K. CuCTAB/MgO calcined at 573 K had a humped peak at similar positions, with a broader peak at approximately 540 K. CuCTAB/MgO calcined at 773 K displayed a different spectrum, with two peaks at 585 K and 660 K. A similar trend was observed for the catalyst calcined at 973 K, which had a peak at 575 K and a shoulder at 620 K. In general, the signals at lower temperatures are due to the easily reducible species in the sample, whereas the signals at higher temperatures indicate species that are harder to reduce. According to the trend in Fig. 7, with increases in calcination temperature, the Cu species in the sample gradually transform into a stable, single species that requires high temperatures to be reduced. The peaks observed at 680 K were attributed to the spinel (or mixed oxide) type species and could not be traced after calcination at higher temperatures, as described by Nagaraja et al. for the Cu/MgO-SSW type catalyst [36]. Such species are considered to be responsible for the unknown peaks in the PXRD and TPR profiles at lower calcination temperatures.

From the TEM images of the copper catalyst (Fig. S2), we can identify that the copper is well dispersed in the non-calcined form and thus can be easily reduced. In contrast, the calcination at higher temperature induces a strong interaction between the metal and the support making it more difficult for them to be reduced at
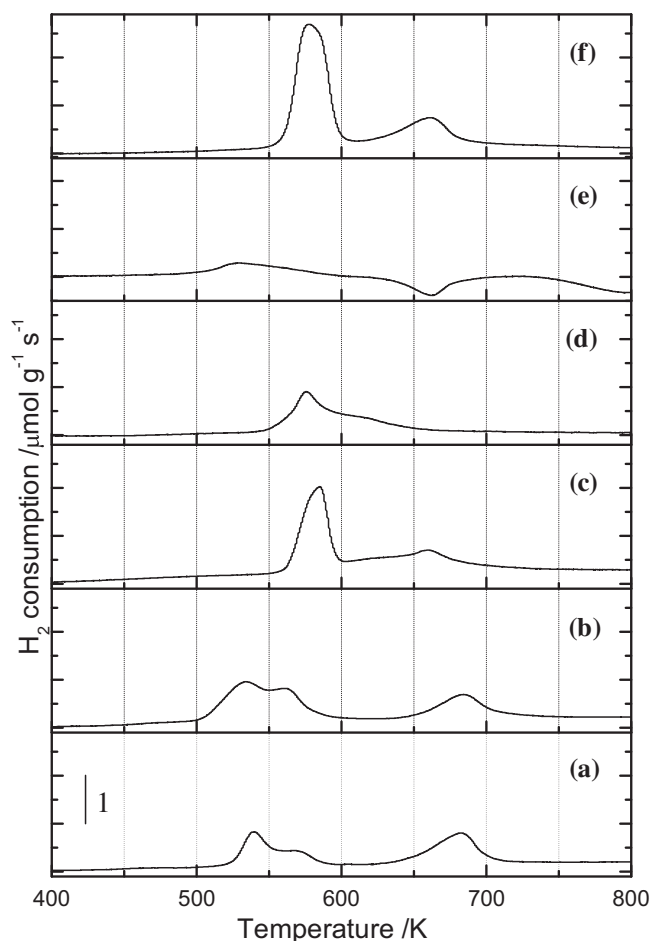
Fig. 7. H_2-TPR profiles of fresh and used 1CuCTAB/MgO catalysts. (a) Non-calcined CuCTAB/MgO; CuCTAB/MgO calcined at (b) 573 K, (c) 773 K and (d) 973 K; (e) CuCTAB/MgO calcined at 773 K after 1st use of glucose to LA; (f) CuCTAB/MgO calcined at 773 K after reactivation.

lower temperatures. Some previous studies have suggested that smaller CuO clusters and/or isolated ionic copper can be reduced at lower temperatures than the larger CuO particles [38]. Thus, the peak above 550 K was related to the reduction of the larger CuO particles. Various studies have reported similar TPR profiles for different supported copper catalysts and have demonstrated the effect of the interaction between the supports and the redox properties of the copper oxide [37b–d, 38–39]. Interestingly, the H_2-TPR profile for the spent catalyst failed to produce any peak, meaning that the spent catalyst did not consume any H_2 gas (Fig. 7e). This observation suggests that the Cu oxide species present in the fresh catalyst was reduced into metal species during the sugar transformation, indicating the reducing nature of the saccharides under the reaction conditions for LA synthesis. The H_2-TPR results for CuCTAB/MgO calcined at 773 K after reactivation were more interesting as they unveiled the hidden Cu species in the catalyst (Fig. 7f) because the reduction of this reactivated catalyst required greater H_2 consumption compared with the fresh catalyst (Fig. 7c), which indicates that the fresh catalyst contained some copper metal species along with the copper oxide species. After the reaction, when the catalyst was reactivated at 773 K, all copper species turned into oxide species, which required increased amounts of H_2 to be reduced to the metallic state.

The PXRD and H_2-TPR studies indicated the presence of unstable phases in both the non-calcined catalyst and the catalyst calcined at 383 K and 573 K. The presence of unstable species in these catalysts is considered the reason for their low activity. With further

increases in calcination temperature (greater than 700 K), the MgO phase becomes more prominent, and the crystallinity of the catalyst is increased, diminishing the catalytic activity. As discussed above, the H_2-TPR studies suggest the presence of easily reducible Cu species in the non-calcined catalyst or in the catalyst calcined at lower temperatures. In addition, the loaded metal species was reduced after the reaction, in accordance with the results of previous studies [26,29]. In general, easily reducible Cu species should be more active for this glucose transformation; however, in the present case, the presence of both oxide and spinel type (or mixed oxide) phases diminishes the amount of easily accessible copper species for the substrate, leading to low activity for the non-calcined CuCTAB/MgO (Fig. 1). CuCTAB/MgO calcined at 773 K was found to be the most active catalyst, with copper oxide interacting strongly with MgO (shown in the N_2 adsorption isotherm, see comments in Tables S3 and Fig. S7). The observed shake-up peaks (in XPS of Cu 2p) and Raman shift also indicate active Cu oxide species (see Figs. S8 and S9).

3.3. Mechanistic considerations

Previous studies have proposed the mechanistic pathways for organic acid production from sugars under hydrothermal conditions [18,25a,26,28,31]. Recently, the role of copper in the deconstruction of sugars has also been studied by Mariani et al. [29]. The general reaction progress of LA synthesis affords various intermediates or by-products such as GlycAld, GlycA, AA, GlcoA, DHA, PAL, and FA. A careful and minute analysis of the experimental evidence helped to propose a plausible mechanistic pathway as Scheme 2 for glucose conversion to LA. In the initial stages, the alkali and/or the catalyst dissect the sugars to GlycAld and DHA. An equilibrium exists between GlycAld and DHA via 1,2,3-propenetriol. Under the present reaction conditions, we could not detect DHA at any stage of the reaction, indicating the shift of keto-enol tautomerism toward GlycAld, which was observed along with GlycA (see Fig. S1). The next intermediate candidate is PAL by dehydration and rearrangement of GlycAld, which thereafter undergoes a methyl shift to generate LA [28]. However, no PAL was observed in the presence of the copper catalyst under our reaction conditions. The adsorption of PAL onto the catalyst surface and the formation of a catalyst–PAL complex (I, Scheme 2) might be responsible for such observations. Additionally, a HPLC chromatogram of the reactions in the absence of the copper catalyst shows trace amounts of PAL (see Fig. S1), which suggests the conversion of GlycAld to PAL as the rate-determining step [9c,40]. The hydrothermally loaded copper oxide species interacts strongly with the support (concluded from the H_2-TPR), which prevents the formation of free cationic copper, as reported by Wang et al. [26]. The attack of the OH^- ion of alkali (indicated by the black arrow) or the binding oxygen atom of Cu–O–Mg from the catalyst (indicated by the red arrow) on the carbonyl carbon may generate II or III.

The formation step of III generates a reduced Cu species as indicated by the characterization data for the spent catalyst. Following this step, the donation of electrons from the oxygen atom forces the methyl group to migrate to the nearest carbon to produce IV or V. The hydrolysis of such complexes yields free LA, representing the role of water as the solvent. Because no free cationic species is generated, the reason for the absence of leaching of the catalyst was addressed. We assume that both II and III are formed in the reaction as intermediates, with III being more likely because the reduced species of Cu were observed after the catalytic run for the LA synthesis. The Brønsted basicity of the catalyst or the medium plays a crucial role because of the need for a base in various steps in the reaction pathway, such as hydrolysis, isomerization, the retro-aldol reaction and the transformation of I into IV and/or V.
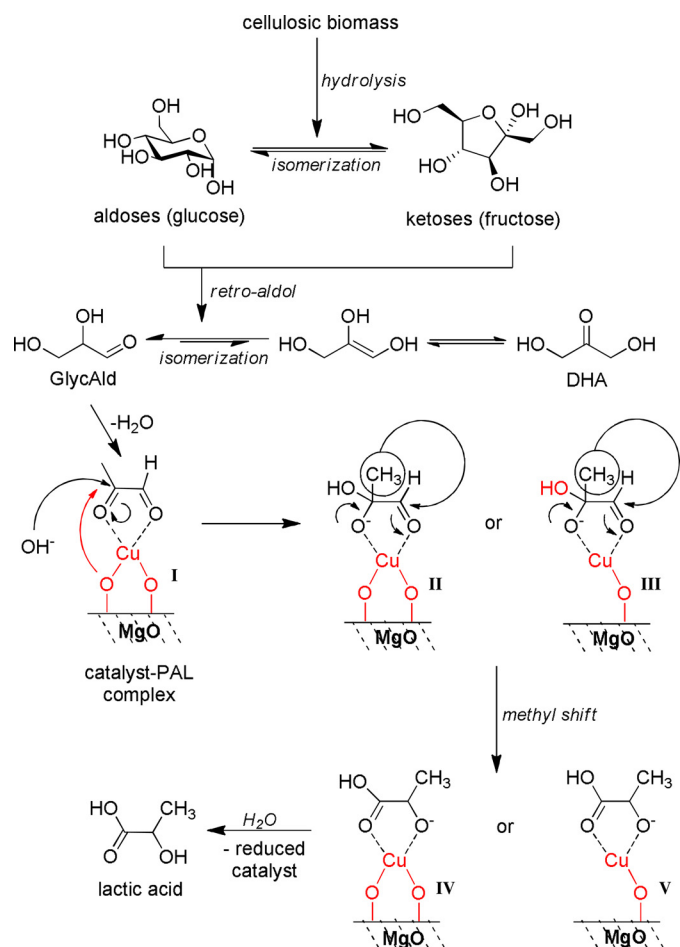
Scheme 2. Proposed Cu-catalyzed pathway for glucose conversion into LA in the presence of alkali.

The oxidative mechanisms for FA formation from sugars are proposed in accordance with Jin et al., assuming a direct oxidation pathway in which six moles of FA are produced per mole of glucose [41]. This mechanism supports the formation of FA in higher yields with increasing amounts of 30% H_2O_2, as discussed above [42]. The copper-loaded catalyst not only influences the FA yield but also has a substantial effect on the activation of 30% H_2O_2 for the oxidation of sugars. Therefore, the use of large amounts of catalyst increases the dissociation of H_2O_2, which increases the FA yield (Table 1, entry 8).

4. Conclusions

In conclusion, hydrothermally loaded copper oxide species on magnesia with a CTAB agent (CuCTAB/MgO) acts as a stable heterogeneous catalyst, which could afford high yields of LA and FA under less extreme reaction conditions. The use of 1CuCTAB/MgO along with NaOH (2.5 M, 1 mL) provided 70% LA yield from glucose at 393 K for 1 h in water. We also found that 0.3CuCATB/MgO catalyst in the presence of aqueous 30% H_2O_2 produced 65% FA yields from glucose at 393 K after 12 h. This catalytic system possessed the advantages of high yields, lower energy input, recyclability of the catalyst and wide scope for various sugars. The characterization of the synthesized catalyst revealed the effect of calcination on the nature of the species in the catalyst. The high selectivity of LA in the presence of the copper catalyst was explained by proposing a plausible mechanism.

The advantages of the above-discussed process seem to have promising potential for bio-refineries and for future sustainability. In the future, the catalyst will be finely adapted to ensure the conversion of polysaccharides and real biomass such as municipal waste with a high carbon balance. Further investigation of the catalyst and its reaction analysis are also needed to propose a suitable mechanism for FA formation. To our knowledge, this is the first report of such high efficiencies for alkaline conversion of sugars into LA and FA under less extreme conditions.

Associated content

The characterization of catalysts (PXRD, TEM, XAFS, XPS, Raman, and Adsorption isotherms), HPLC chromatograms and reaction optimization data are included.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2014.05.012.

References

[1] For example;
(a) A. Corma, S. Iborra, A. Velty, Chem. Rev. 107 (2007) 2411–2502;
(b) D.M. Alonso, S.G. Wettstein, J.A. Dumesic, Chem. Soc. Rev. 41 (2012) 8075–8098;
(c) H. Kobayashi, A. Fukuoka, Green Chem. 15 (2013) 1740–1763;
(d) Y. Nakagawa, M. Tamura, K. Tomishige, ACS Catal. 3 (2013) 2655–2668.
[2] (a) J.C. Serrano-Ruiz, R. Luque, A. Sepulveda-Escribano, Chem. Soc. Rev. 40 (2011) 5266–5281;
(b) P.Y. Dapsens, C. Mondelli, J. Perez-Ramirez, ACS Catal. 2 (2012) 1487–1499;
(c) A. Takagaki, S. Nishimura, K. Ebitani, Catal. Surv. Asia 16 (2012) 164–182.
[3] (a) M. Bicker, J. Hirth, H. Vogel, Green Chem. 5 (2003) 280–284;
(b) A. Takagaki, M. Ohara, S. Nishimura, K. Ebitani, Chem. Commun. 45 (2009) 6276–6278;
(c) T. Stahlberg, W. Fu, J.M. Woodley, A. Riisager, ChemSusChem 4 (2011) 451–458;
(d) J. Tuteja, S. Nishimura, K. Ebitani, Bull. Chem. Soc. Jpn. 85 (2012) 275–281;
(e) I.-J. Kuo, N. Suzuki, Y. Yamauchi, K.C.-W. Wu, RSC Adv. 3 (2013) 2028–2034;
(f) I. Jimenez-Morales, A. Teckchandani-Ortiz, J. Santamaria-Gonzalez, P. Maireles-Torres, A. Jimenez-Lopez, Appl. Catal. B 144 (2014) 22–28.
[4] (a) M. Chidambaram, A.T. Bell, Green Chem. 12 (2010) 1253–1262;
(b) Y. Zu, P. Yang, J. Wang, X. Liu, J. Ren, G. Lu, Y. Wang, Appl. Catal. B 146 (2014) 244–248;
(c) S. Nishimura, N. Ikeda, K. Ebitani, Catal. Today 232 (2014) 89–98.
[5] (a) G.A. Halliday, R.J. Young Jr., V.V. Grushin, Org. Lett. 5 (2003) 2003–2005;
(b) A. Takagaki, M. Takahashi, S. Nishimura, K. Ebitani, ACS Catal. 1 (2011) 1562–1565;
(c) G.D. Yadav, R.V. Sharma, Appl. Catal. B 147 (2014) 293–301.
[6] (a) C. Delhomme, D. Weuster-Botz, F.E. Kühn, Green Chem. 11 (2009) 13–26;
(b) H. Choudhary, S. Nishimura, K. Ebitani, Chem. Lett. 41 (2012) 409–411;
(c) H. Choudhary, S. Nishimura, K. Ebitani, Appl. Catal. A 458 (2013) 55–62.
[7] (a) R. Weingarten, J. Cho, R. Xing, W.C. Corner Jr., G.W. Huber, ChemSusChem 5 (2012) 1280–1290;

(b) P.A. Son, S. Nishimura, K. Ebitani, React. Kinet. Mech. Catal. 106 (2012) 185–192.

[8] (a) M.J. Climent, A. Corma, S.B.A. Hamid, S. Iborra, M. Mifsud, Green Chem. 8 (2006) 524–532;
(b) T. Miyake, T. Makino, S. Taniguchi, H. Watanuki, T. Niki, S. Shimizu, Y. Kojima, M. Sano, Appl. Catal. A 364 (2009) 108–112;
(c) E.J. Steen, Y. Kang, G. Bokinsky, Z. Hu, A. Schirmer, A. McClure, S.B. del Cardayre, J.D. Keasling, Nature 463 (2010) 559–562.

[9] (a) M.S. Holm, S. Saravanamurugan, E. Taarning, Science 328 (2010) 602–605;
(b) F. Chambon, F. Rataboul, C. Pinel, A. Cabiac, E. Guillon, N. Essayem, Appl. Catal. B 105 (2011) 171–181;
(c) F. Clippel, M. Dusselier, R.V. Rompaey, P. Vanelderen, J. Dijkmans, E. Makshina, L. Giebeler, S. Oswald, G.V. Baron, J.F.M. Denayer, P.P. Pescarmona, P.A. Jacobs, B.F. Sels, J. Am. Chem. Soc. 134 (2012) 10089–10101;
(d) D. Tongsakul, S. Nishimura, K. Ebitani, ACS Catal. 3 (2013) 2199–2207;
(e) R.K.P. Purushothaman, J. van Haveren, D.D. van Es, I. Melian-Cabrera, J.D. Meeldijk, H.J. Heeres, Appl. Catal. B 147 (2014) 92–100.

[10] (a) G.-Q. Chen, M.K. Patel, Chem. Rev. 112 (2012) 2082–2099;
(b) F.A.C. Martinez, E.M. Balciunas, J.M. Salgado, J.M.D. Gonzalez, A. Converti, R.P.S. Oliveira, Trends Food Sci. Technol. 30 (2013) 70–83.

[11] (a) A. Boddien, D. Mellmann, F. Gartner, R. Jackstell, H. Junge, P. Dyson, G. Laurenczy, R. Ludwig, M. Beller, Science 333 (2011) 1733–1736;
(b) Q.-Y. Bi, X.-L. Du, Y.-M. Liu, Y. Cao, K.-N. He, K.-N. Fan, J. Am. Chem. Soc. 134 (2012) 8926–8933;
(c) M. Grasemann, G. Laurenczy, Energy Environ. Sci. 5 (2012) 8171–8181;
(d) J. Tuteja, H. Choudhary, S. Nishimura, K. Ebitani, ChemSusChem 7 (2014) 96–100;
(e) P.A. Son, S. Nishimura, K. Ebitani, RSC Adv. 4 (2014) 10525–10530.

[12] (a) R.P. John, K.M. Nampoothiri, A. Pandey, Appl. Microbiol. Biotechnol. 74 (2007) 524–534;
(b) K. Okano, T. Tanaka, C. Ogino, H. Fukuda, A. Kondo, Appl. Microbiol. Biotechnol. 85 (2010) 413–423.

[13] E.J. Ordal, H.O. Halvorson, J. Bacteriol. 38 (1939) 199–220.

[14] S.P. Chahal, Lactic Acid in Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co., Germany, 2000, pp. 11–19.

[15] W. Reutemann, H. Kieczka, Formic Acid in Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co., Germany, 2011, pp. 49–70.

[16] S.K. Hoekman, A. Broch, C. Robbins, Energy Fuels 25 (2011) 1802–1810.

[17] P.A. Shaffer, T.E. Friedemann, J. Biol. Chem. 86 (1930) 345–374.

[18] H. Kishida, F. Jin, X. Yan, T. Moriya, H. Enomoto, Carbohydr. Res. 341 (2006) 2619–2623.

[19] X. Yan, F. Jin, K. Tohji, A. Kishita, H. Enomoto, AIChE J. 56 (2010) 2727–2733.

[20] D. Esposito, M. Antonietti, ChemSusChem 6 (2013) 989–992.

[21] P. Gao, G. Li, F. Yang, X.-N. Lv, H. Fan, L. Meng, X.-Q. Yu, Ind. Crops Prod. 48 (2013) 61–67.

[22] F. Jin, J. Yun, G. Li, A. Kishita, K. Tohji, H. Enomoto, Green Chem. 10 (2008) 612–615.

[23] A. Onda, T. Ochi, K. Kajiyoshi, K. Yanagisawa, Catal. Commun. 9 (2008) 1050–1053.

[24] S. Zhang, F. Jin, J. Hu, Z. Huo, Bioresour. Technol. 102 (2011) 1998–2003.

[25] (a) M. Bicker, S. Endres, L. Ott, H. Vogel, J. Mol. Catal. A 239 (2005) 151–157;
(b) L. Kong, G. Li, H. Wang, W. He, F. Ling, J. Chem. Technol. Biotechnol. 83 (2008) 383–388.

[26] Y. Wang, F. Jin, M. Sasaki, F. Wahyudiono, Z. Wang, M. Jing, Goto, AIChE J. 59 (2013) 2096–2104.

[27] (a) M. Tada, R. Bal, X. Mu, R. Coquet, S. Namba, Y. Iwasawa, Chem. Commun. 44 (2007) 4689–4691;
(b) B. Sarkar, P. Prajapati, R. Tiwari, R. Tiwari, S. Ghosh, S.S. Acharyya, C. Pendem, R.K. Singha, L.N.S. Konathala, J. Kumar, T. Sasaki, R. Bal, Green Chem. 14 (2012) 2600–2606;
(c) S.S. Acharyya, S. Ghosh, R. Bal, ACS Sustain. Chem. Eng. 2 (2014) 584–589.

[28] A.V. Ellis, M.A. Wilson, J. Org. Chem. 67 (2002) 8469–8474.

[29] M. Mariani, F. Zaccheria, R. Psaro, N. Ravasio, Catal. Commun. 44 (2014) 19–23.

[30] A.T. Quitain, M. Faisal, K. Kang, H. Daimon, K. Fujie, J. Hazard. Mater. 93 (2002) 209–220.

[31] F. Jin, H. Enomoto, Energy Environ. Sci. 4 (2011) 382–397.

[32] (a) N. Akiya, P.E. Savage, AIChE J. 44 (1998) 405–415;
(b) J. Yu, P.E. Savage, Ind. Eng. Chem. Res. 37 (1998) 2–10.

[33] The GC analysis of the gaseous products showed the absence of both H_2 and CO_2 (dissociation products of FA), indicating the transformation of FA to carbonates or bicarbonates under longer reaction times.

[34] The activity of the catalyst for soluble starch (90 mg) was observed to produce 11.4 mg of LA (in the presence of 1 M NaOH) and 40.7 mg of FA (in the presence of 2 mmol 30% H_2O_2). Because of the uncertainty in the molecular mass of the starch, the yields of LA and FA could not be calculated.

[35] Some unknown peaks at 2θ values of 19.1, 38.4, and 51.3 were observed for low calcination temperatures, which subsequently disappeared at higher temperatures. These peaks are assigned to the highly crystalline Cu-Mg spinel type (or mixed oxide) formed during the catalyst synthesis as reported by Nagaraja et al. [36]. This could also explain the absence of crystalline MgO in the PXRD patterns for the catalyst treated at lower temperatures.

[36] B.M. Nagaraja, V.S. Kumar, V. Shashikala, A.H. Padmasri, S.S. Reddy, B.D. Raju, K.S.R. Rao, J. Mol. Catal. A 223 (2004) 339–345.

[37] (a) H.-P. Wang, C.-T. Yeh, J. Chin. Chem. Soc. 30 (1983) 139–143;
(b) L. Kundakovic, M.-F. Stephanopoulos, Appl. Catal. A 171 (1998) 13–29;
(c) M. Vijayaraj, C.S. Gopinath, J. Catal. 241 (2006) 83–95;
(d) S. Nishimura, T. Shishido, J. Ohyama, K. Teramura, A. Takagaki, T. Tanaka, K. Ebitani, Catal. Sci. Technol. 2 (2012) 1685–1693.

[38] R. Rajeev, K.A. Devi, A. Abraham, K. Krishnan, T.E. Krishnan, K.N. Ninan, C.G.R. Nair, Thermochim. Acta 254 (1995) 235–247.

[39] E. Moretti, M. Lenarda, L. Storaro, A. Talon, T. Montanari, G. Busca, E. Rodriguez, A. Jimeenez, M. Turco, G. Bagnasco, Appl. Catal. A 335 (2008) 46–55.

[40] C.B. Rasendra, B.A. Fachri, I. Gusti, B.N. Makertihartha, S. Adisasmito, H.J. Heeres, ChemSusChem 4 (2011) 768–777.

[41] F. Jin, Z. Zhou, T. Moriya, H. Kishida, H. Higashijima, H. Enomoto, Environ. Sci. Technol. 39 (2005) 1893–1902.

[42] For the production mechanism of FA from glucose in the presence of H_2O_2, see H.S. Isbell, R.G. Naves, Carbohydr. Res. 36 (1974) C1–C4.